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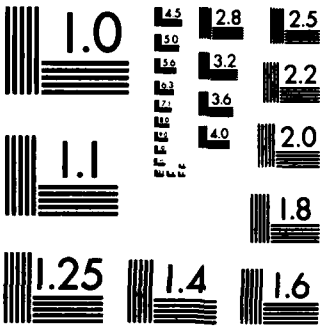

FINAL REPORT

PHOTOIONIZATION INVESTIGATION OF IODINE MOLECULES AND CLUSTERS IN A SUPERSONIC MOLECULAR BEAM

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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

A nozzle was designed and constructed which is to produce clusters of iodine molecules in the gas phase. Preliminary tests were conducted. A partial photoion yield curve for the production of iodine molecular ions was obtained for the wavelength region of 1216-1254 Å and 1299-1346 Å at an optical resolution of 1.75 Å. The adiabatic ionization potential of molecular iodine was determined to be 9.308±0.006 eV with a spin-orbit splitting to the next highest electronic energy state of 0.645±0.006 eV. Many autoionization features were observed, but because of the limited range of the wavelength study they were not assigned (over

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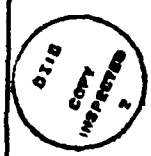

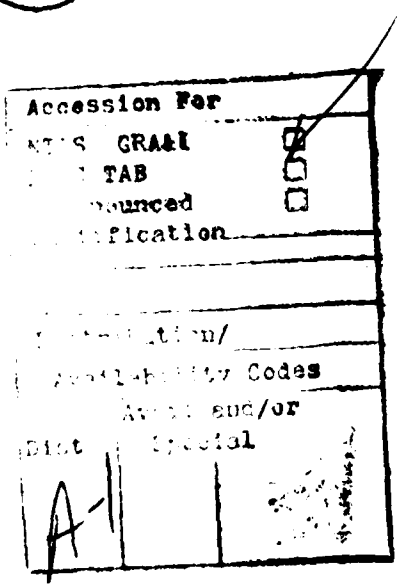

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INTRODUCTION

The oxygen-iodine laser operates on a process of energy migration from excited oxygen to atomic iodine. The excited oxygen molecular oxygen in the singlet state, $O_2(^1\Delta)$. There are two common ways of generating $O_2(^1\Delta)$. First, excited oxygen is produced in low, but usable, concentrations when a mixture of O_2 in He is passed through a microwave discharge at 2450 MHz. Alternatively, it is the product of the reaction between Cl_2 and a mixture of NaOH and H_2O_2. This latter route provides a chemical pathway to pumping the iodine laser and consequently presents many attractive possibilities.

The lasers that have been constructed to date have been almost exclusively small-scale devices in which I_2 is injected into a cavity containing $O_2(^1\Delta)$. The net result of this interaction is the generation of I*, but the mechanism by which this occurs is known only vaguely. It is generally believed that the reaction consists of at least two steps, the dissociation of I_2 by $O_2(^1\Delta)$ to give I atoms followed by excitation of I to I* by more $O_2(^1\Delta)$. This however is not at all clear. Nevertheless, if the laser is to be scaled from a "bench-top" model to something larger, the order and mechanism of the reactions must be understood to assure proper scaling.

The first reported work on I_2 dissociation by $O_2(^1\Delta)$ was by Derwent, Kearns, and Thrush (1). In addition to the evidence of emission from atomic iodine they noticed a yellow glow which was attributed to the I_2 molecular transition $B^3\pi_{0^+u} \rightarrow X^1\Sigma$. The mechanism they suggested which was compatible with their results is

Chief, [illegible] Division

$$O_2(^1\Sigma) + I_2(X^1\Sigma) \rightarrow O_2(^3\Sigma) + 2I$$

$$O_2(^1\Sigma) + I_2(X^1\Sigma) \rightarrow O_2(^3\Sigma) + I_2(A^3\pi_{1u})$$

$$I_2(A^3\pi_{1u}) + O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + I_2(B^3\pi_{0^+u})$$

The serious flaw with this mechanism is that I* atoms are produced in the chemically pumped reaction and that under these conditions sufficient H_2O is present to quench all $O_2(^1\Sigma)$ before reaction with I_2 is possible. This was confirmed by experiments in which I* was produced in the absence of $O_2(^1\Sigma)$ (2). Thus the only other excited species, $O_2(^1\Delta)$, must be responsible for the dissociation and energetics requires at least two of these molecules. A number of possible mechanisms are currently under investigation, but they are all still quite speculative and very little information is available which even favors such a mechanism as, say, one involving vibrationally excited $O_2(^1\Delta)$ or the theoretically predicted but experimentally unknown dark state of $I_2(A'^3\pi_{2u})$.

In order to minimize the quenching effects of all the compounds found in the chemically pumped laser and thereby produce efficient cw operation of the oxygen-iodine laser it is important to remove the products as quickly as possible from the active volume. Ideally, this may be accomplished by rapid mixing of the reactants $O_2(^1\Delta)$ and I. In order to obtain high cw power levels it is necessary that the gas flow velocities be supersonic. In the case of the HF/DF laser this is done by injecting H_2 or D_2 through nozzles into an expanding flow of F atoms in an appropriate carrier gas. Unlike the HF/DF system, for which a large amount of practical data are at hand, the problems of mixing a very massive molecule like I_2 into a relatively light gas of O_2 molecules have not been resolved to say nothing of the generation

of a beam of atomic iodine. The low cross section for stimulated emission also dictates that the mole fraction of iodine be high. It is evident therefore that supersonic mixing introduces a number of other unanswered questions into the operation of the oxygen-iodine laser.

There are more questions related to the basic chemistry of the laser. For example, in a clean system of I atoms and $O_2(^1\Delta)$ molecules only the four following reactions are needed to describe the observed kinetics (3);

$$O_2(^1\Delta) + I \leftrightharpoons O_2(^3\Sigma) + I^*$$

$$I^* + O_2(^1\Delta) \rightarrow I + O_2(^1\Sigma)$$

$$I^* + O_2(^3\Sigma) \rightarrow I + O_2(^3\Sigma)$$

$$O_2(^1\Delta) + O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + O_2(^1\Sigma)$$

Although there do exist data on all of these reactions, it is relatively incomplete and, in fact, there is considerable uncertainty about the $I^* + O_2(^3\Sigma)$ reaction.

In a real system there will be contaminants in the flow, principally H_2O and Cl_2; rates of reactions of these species with I^* and $O_2(^1\Delta)$ are not well known.

Iodine recombination rates are also critical (3). The reaction rates are known for the three-body process

$$I + I + I_2 \rightarrow 2I_2$$

at room temperature to 1000°K and atmospheric pressure. Extrapolation to temperatures of 100-200 K, as encountered in supersonic nozzle expansions, is very uncertain except for the knowledge that the three-body rate increases as the temperature decreases. Some reasonable extrapolations suggest that at the low temperatures this reaction may be very troublesome.

Finally, cluster formation is a well-known phenomenon in supersonic nozzle expansions. The possibility of the formation of small metastable clusters in reactions such as

$$I + I_2 \rightarrow I_3$$

need to be explored. There is reason to believe that I_3 is bound; if so, the reaction resulting in its formation will be a channel for depletion of the I atoms needed for producing high energy laser emission. Alternatively, clusters could be a source of additional iodine atoms. This is but one of several broader questions related to cluster formation and nucleation phenomena in a supersonic oxygen-iodine laser.

We report here on our efforts to generate the simplest iodine atom cluster, $I \cdot I_2$, and to study the photoionization behavior of both I_2 and the cluster. First, a nozzle was designed and constructed for use in a molecular beam sampling source photoionization mass spectrometer for the purpose of producing I atom clusters. Next, the partial photoion yield curve of I_2 cooled in a supersonic nozzle expansion was determined. The results are discussed below.

The absorption spectrum of the iodine molecule has been studied extensively over a period of many years. The great majority of this work has concentrated on the region above 1700 Å and surprisingly little has been done in

the vacuum-UV region below this value. There are several reasons for this. First, autoionization features are dominant from threshold into the far UV thereby making identification of vibrational progressions and ionization to excited states difficult. In addition, the close spacing of the vibrational levels of I_2, 214 cm^{-1}, means that at 300 K there is considerable population of the v=2 and v=3 levels, so hot bands obscure the ionization threshold and other vibrational sequences. The ionization potential has been determined by vuv spectroscopy (4), electron impact ionization (5), photoelectron spectroscopy (6-9), photoionization without mass selection (10-12) and photoionization with mass analysis (12,13). Photoion yield curves for the region of 1050 to 1410 Å (10,13) have been published. In the first instance (10) only total ion current was measured, so the rather prominent structures at lower energy than the spectroscopic ionization potential of 9.400 eV (4) were attributed to the ion-pair formation

$$I_2 + h\nu \rightarrow I_2^* \rightarrow I^+ + I^-.$$

The threshold for this process was measured as 8.84 eV. This corresponds well with the earlier results of Morrison et al. (12) and Watanabe (14) who give 8.85±0.1 eV and 8.93±9.02 eV, respectively, as the onsets for ion-pair production. Ionization potentials for I_2 have been established from these reports as being close to 9.38 eV.

EXPERIMENTAL

Iodine Atom Cluster Nozzle

A detailed drawing of the nozzle constructed is shown in Figure 1. The nozzle was designed for mounting in the existing photoionization mass spectrometer at the University of New Mexico. The nozzle body is constructed of nickel and the tubing is stainless steel. With use of a copper gasket the entire assembly is metal so it can be heated. In operation a stream of O_2 which passed through a microwave discharge to generate $O_2(\Delta_g)$ enters the outer housing and a flow of He containing I_2 passes through the inner tube. In the region between the inner and outer nozzles the processes take place which result in the formation of I atoms. In the subsequent expansion it can be expected that collisions between I and I_2 will yield small quantities of the van der Waals molecule $I \bullet I_2$. The nozzle was designed in this manner so that a steady pressure drop would occur from the inner tubing containing He and I_2 to the expansion chamber. Typical operating pressures are 200 Torr He (with a small amount of I_2) in the innermost tube, 10^{-1} Torr O_2 in the next tube and 10^{-3} Torr beyond the nozzle in the expansion regime. Provisions were made for heating the nozzle if it were found that the room temperature vapor pressure of I_2 (0.35 Torr) is too low to yield sufficient count rates to characterize the products.

The nozzle was assembled and tests were run in a bell-jar type vacuum chamber. These tests however were limited to passing a stream of He + I_2 through the inner tube while varying the pressure of a gas, in this case only He, in the outer cylinder due to time constraints.

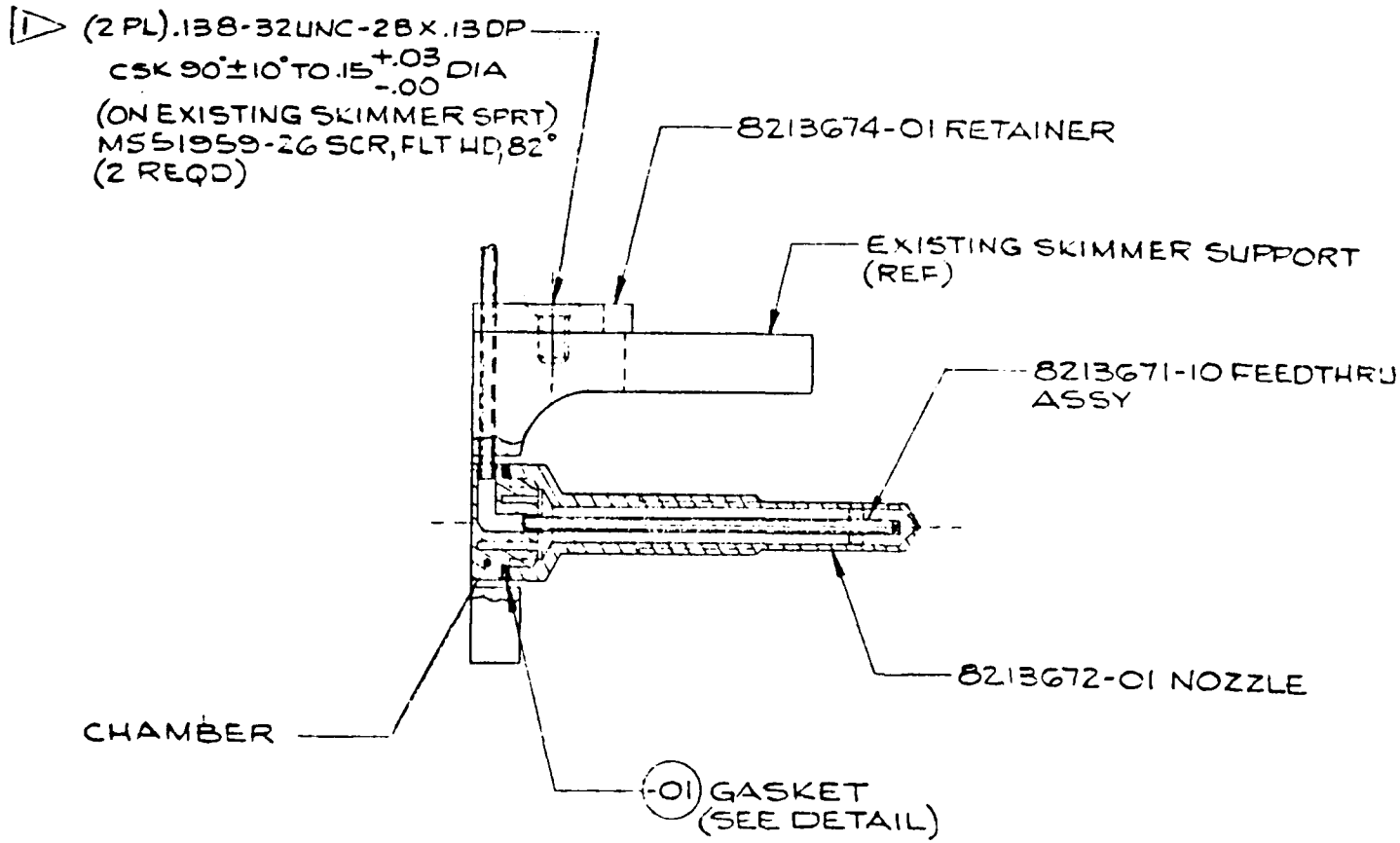
Photoionization Efficiency (PIE) Curve for I_2

The experimental procedure used in obtaining the photoionization efficiency (PIE) curve for species has been described in detail elsewhere (15). The techniques employed in this experiment were fundamentally the same however it was necessary to install a considerable amount of inlet line heating equipment due to the low volatility of I_2. A number of methods for vaporizing I_2 were attempted. First, a cylindrical glass cell with o.d. = 1 inch was constructed. It had an inlet for He on one side and an outlet on the other. The top was a 2-mm thick window of NaCl. I_2 was vaporized by heating I_2 crystals at the bottom of the cell by means of an infrared heat lamp. The second technique was a variation on this in which the cell was replaced by a 4-inch long, 3/4-inch o.d. length of Pyrex tubing. I_2 crystals were distributed along the bottom and the entire length was heated with an ir lamp. In the third method a 2-inch length of 3/4-inch o.d. stainless steel tubing served as the I_2 source. This was packed with I_2 crystals mixed with glass wool which was inserted for improved heat distribution. This cell was heated externally by electrically controlled heat tapes. It was essential to preheat the He carrier gas and to use a coarse stainless steel frit downstream from the cell to prevent particles from being carried into the nozzle.

For this experiment the simple nozzle used previously (15-17) was employed.

The wavelength scale was calibrated against the known lines in the hydrogen discharge spectrum and the mass spectrometer was calibrated by the ionization of Xe under electron impact ionization conditions. The known isotope distribution permitted unambiguous determination of the mass numbers at the higher mass numbers required for this experiment. Monochromator entrance and exit slit widths were 100 μm.

Figure 1. Cross-sectional view of the supersonic nozzle designed for the production of I atom clusters.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MS51959-26 SCR, FLT HD, 82°
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8213674-01 RETAINER
EXISTING SKIMMER SUPPORT
(REF)
8213671-10 FEEDTHRU
ASSY
8213672-01 NOZZLE
CHAMBER
-01 GASKET
(SEE DETAIL)

Figure 1

RESULTS AND DISCUSSION

Iodine Atom Cluster Nozzle.

The nozzle described above was assembled and studied in a test stand. The basic design of this nozzle appears to require modification because it was never possible to get a satisfactory beam of I_2 molecules into the expansion region. There are several problems, all of which can be surmounted by improvements in the design. The first problem has to do with adequate heating of the innermost tube. The principal difficulty here is uneven distribution of heat with the consequent buildup of I_2 crystals in cold spots leading to nozzle plugging. In our apparatus the nozzle is supported in a block of boron nitride which is resistively heated by nichrome wire fed through the block. The outer cylinder contacts this block in two places, one near the top and the other near the base. The inner nozzle seems to be too far removed from a warm surface to allow adequate and even distribution of heat so that nozzle clogging was a severe problem.

A second difficulty with the present design is interference from the gas in the mixing chamber. As described in the experimental section this study was restricted to the use of He in this chamber. The pressure of He in the line leading to this region was varied from 10^{-3}-1 Torr while the pressure in the innermost tube was maintained at 200 Torr. At low pressures, the beam from the nozzle was of low intensity probably due to the extremely high tolerances required to match the nozzle of the interior tube with that of the outer one which in this case served as a skimmer. A solution to this problem would be to enlarge the opening into the expansion chember so alignment would not be so critical. Time did not permit this alteration.

At the higher pressures a beam emerged whose I_2 composition diminished sharply with increasing pressure. This effect is due to choking of the beam

from the internal nozzle by the He which serves as a buffer.

There exists an intermediate pressure range in which it appears that this nozzle arrangement may give the desired results, however the detection system on the test stand was inadequate for thorough characterization of the nozzle. Installation of the nozzle in the photoionization apparatus was not made due to unsolved difficulties encountered in producing the simple I_2 beam to be described below. A more desirable technique for characterizing the nozzle would be laser induced fluorescence. The photoionization method requires a rather intense beam of I_2 to give counting rates needed to clearly define the performance of the nozzle. Such intense beams are not needed for the very sensitive detection technique of laser induced fluorescence. I_2 is particularly amenable to detection by this method since it can be used coveniently even with room temperature I_2 in He (18) and it exhibits strong, characteristic fluorescence in the visible region of the spectrum.

PIE Curve for I_2.

The low vapor pressure of I_2 caused a number of difficulties in carrying out this experiment. The most satisfactory cell for producing the I_2 beam was the thermally heated stainless steel tube. It was necessary to go to great lengths to heat the entire inlet line, especially in the vicinity of any connections. We were regularly troubled with condensation of I_2 crystals in any portion of the inlet system that was inadequately heated.

The technique of molecular beam photoionization requires rather large amounts of I_2. Much of this is pumped away in the chamber immediately outside the nozzle, but the large quantities are required to get enough molecules into the ionization region to allow high enough counting rates of the I_2^+ product ions to give statistically significant results in a

reasonable counting time. The amounts of I_2 introduced into the apparatus caused a number of operational difficulties due to its proclivity for condensing on all available cool surfaces.

In spite of these problems a partial PIE curve for I_2 was obtained, it is shown in Figure 2. The PIE curve covers the range of 1216-1345 Å with a break from 1254-1299 Å at a resolution of 1.75 Å.

The valence shell ground electronic state electron configuration of the I_2 molecule is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$. Ionization from the outermost $(\pi_g)^4$ and $(\pi_u)^4$ orbitals will produce I_2^+ ions in the $^2\pi_g$ and $^2\pi_u$ states. Each of the $^2\pi$ states will be further split by spin-orbit interaction to give the states $^2\pi_{3/2g}$, $^2\pi_{3/2u}$, $^2\pi_{1/2g}$, $^2\pi_{1/2u}$ the ordering of which depends upon the g-u and Ω = 3/2 and 1/2 separations. Photoelectron spectroscopy (PES) studies of the halogens (2-10,19) have confirmed that the lowest energy band corresponds to the states $X^2\pi_{3/2g}$ and $^2\pi_{1/2g}$ associated with ionization of an antibonding π electron in the neutral molecule. Removal of an antibonding electron should result in an I_2^+ ion with a shorter internuclear separation than in the neutral. Potts and Price (19) used the shapes of the PES curves to estimate potential energy curves for the ion states and found that r_e decreased by 0.08 Å on ionization to the $^2\pi_g$ state. A decrease of this magnitude reflects the low Franck-Condon factor for adiabatic ionization. This effect coupled with the presence of prominent hot bands due to the low vibrational frequency, 213.4 cm^{-1}, of the I_2 molecule has given rise to considerable uncertainty and controversy over the adiabatic IP of I_2.

Since in this experiment we were able to obtain a limited amount of experimental data, we concentrated our effoets on obtaining high resolution

Figure 2. Partial photoion yield curve for the production of I_2^+ in the vicinity of the ionization threshold.

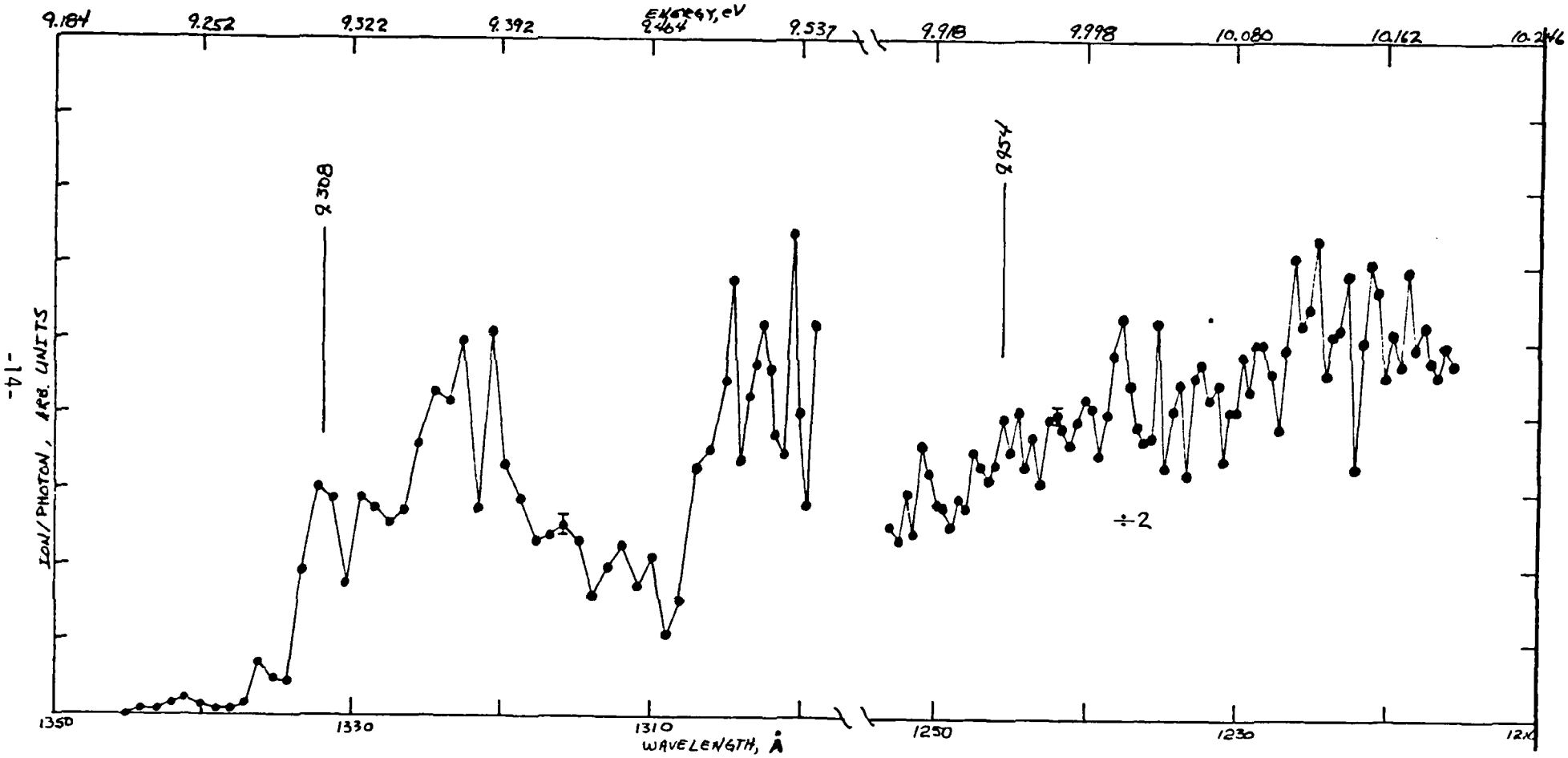
9.184
9.252
9.322
9.392
ENERGY, eV
9.464
9.537
9.918
9.998
10.080
10.162
10.246
9.308
9.954
ION/PHOTON, ARB. UNITS
÷2
1350
1330
1310
WAVELENGTH, Å
1250
1230
1210

Figure 2

PIE information in the vicinity of ionization to the $^2\pi_{3/2g}$ and $^2\pi_{1/2g}$ states of I_2^+ for I_2 molecules cooled in a nozzle expansion. The partial PIE curves of Figure 2 cover these regions.

One of the advantages gained by use of the supersonic nozzle source is dramatic cooling of the I_2 molecules in the beam in spite of the need to operate the I_2 source at elevated temperatures in the first place. The cooling is important in identification of the actual ionization threshold. This has been an outstanding problem for many years (4-10) because of the low vibrational frequency, 213.4 cm^{-1} in neutral I_2. In Figure 2 it is evident that a distinct onset occurs at 1332.0±1.7 Å (9.308±0.006 eV); although two small maxima appear at longer wavelengths we assign the 9.308 eV maximum to the adiabatic ionization of I_2 to the $^2\pi_{3/2g}$ state of I_2^+. The two small peaks are hot bands due to ionization from vibrationally excited I_2. The intensity of the first of these peaks defines it cleanly enough to permit reasonable evaluation of its location. The maximum is found at 239±50 cm^{-1} below the $^2\pi_{3/2g}$ threshold, which is in excellent agreement with the known value of 213.4 cm^{-1}. The IP reported here is consistent with the assignment given by Higginson et al. (9) who used Ne(I) variable temperature photoelectron spectroscopy to determine the adiabatic IP of I_2 as 9.311±0.002 eV.

The spectrum in the vicinity of the $^2\pi_{1/2g}$ onset is considerably more congested due to autoionization features. The Ne(I) PE spectrum does not suffer this problem so a clear identification of the onset has been made (9) at 9.953±0.002 eV. We find a sharp peak at 1245.2±1.7 Å (9.954±0.006 eV) which we identify with the $^2\pi_{1/2g}$ ionization threshold.

The spin-orbit splitting observed here is 5214±50 cm^{-1} (0.645±0.006 eV). This value is consistent with those reported earlier (9,19).

The overall shape of the PIE curve is very similar to that given by Dibeler et al. (13), however the cooling and higher resolution in this work reveals more detail than the earlier study. As can be seen from the error bars (statistical limits obtained from total counts collected at that wavelength) many of the features are statistically significant. Since it was not possible to carry out a thorough study of the PIE curve over the entire wavelength range, we cannot resolve these isolated autoionizaion features into Rydberg series. It is nevertheless important to note that a careful examination of this spectrum shows the anticipated existence of many pairs of maxima separated by 225±50 cm^{-1}. These are evidently due to autoionization from vibrationally excited Rydberg levels of neutral I_2.

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PERSONNEL

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2. Eddie T. Hui, graduate student. Ph.D. expected December, 1984.

CONTACTS

Until 31 October 1983 we had close and frequent contact with Major David E. Ellis, AFWL, KAFB regarding design and construction of the nozzle. At that time he was reassigned to a new post and we have had virtually no communication with Air Force personnel since.